

Atmospheric wet deposition of PAHs to the sea-surface microlayer

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Abstract

Sea-surface microlayer (SML) and subsurface seawater samples (SSW) collected from Singapore's coastal environment were analyzed for 14 polycyclic aromatic hydrocarbons (PAHs) in the dissolved (DP) and suspended particulate phase (SPM). Samples were collected prior to and after rainfall events to ascertain the contribution of wet atmospheric deposition of PAH enrichment to the SML. The concentration ranges of Σ PAHs in the SML before rain and after wet deposition were 2.6–46.2 ng L⁻¹ and 4.3–278.0 ng L⁻¹, respectively, for the DP and 3.8–31.4 ng L⁻¹ and 12.8–1280 ng L⁻¹, respectively, for the SPM. Load factors (i.e. concentration after wet deposition relative to before wet deposition) of the atmospheric wet deposition for DP and SPM ranged from 1.4 to 42.9 and 1.2 to 337, respectively. This study provides the first data on PAH concentration, enrichment (i.e. concentration of PAHs in SML relative to subsurface water) and load factors in the SML before and after wet deposition to the ocean surface.

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1. Introduction

The sea-surface microlayer SML of the ocean represents the boundary layer between the atmosphere and the ocean surface body, and has a typical thickness of 40–100 μ m. The SML is enriched in naturally occurring organic compounds, including proteins, lipids and organic surfactants, giving it a distinct chemical composition (Hardy, 1982; Garabetian et al., 1993; Williams et al., 1986). Anthropogenic contaminants, including persistent organic pollutants (POPs), are known to accumulate in the SML resulting in their enrichment relative to the underlying water column. There is also evidence that flocculated particles floating on the sea-surface may act as an important sink of POPs within the water column of coastal areas (Wurl and Obbard, 2006). Concentration levels and enrichment fac-

tors of POPs in the SML sampled in different parts of the world have been reviewed by Wurl and Obbard (2004). Studies on polycyclic aromatic hydrocarbons (PAHs) in the SML have been conducted in very few regions of the world, with no data for Southeast Asia (Wurl and Obbard, 2004). From previous studies (Wurl and Obbard, 2005), it is known that atmospheric wet deposition during the monsoon season may be a potentially important source of organic contaminants to the SML. Particulates may represent an important medium for the accumulation of contaminants in the SML as shown for PAHs (Guitart et al., 2007) and polychlorinated biphenyls (PCBs) (Wurl and Obbard, 2006). The enrichment of POPs including PAHs in the SML presents a potential threat to both marine biodiversity and commercial fisheries (Cross et al., 1987; Hardy et al., 1987).

Singapore, is an island state located approximately 120 km north of the equator surround by Malaysia in the north and Indonesia in the south. It is a fully industrialized country with one of the world's busiest ports with an annual shipping tonnage of 958 million gross tonnes per year based on the average from 1999 to 2004 which is

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equivalent to more than 140,000 ship movements per year. Singapore is also home to one of the largest petroleum refinery industries in the world. The climate in Singapore is characterized by a tropical climate together with an annual average rainfall of 2345 mm (NEA, 2005) and a mean temperature of about 31 °C.

This study focuses on the measurement of PAHs in the SML and subsurface water (SSW) before and immediately after rainfall events in order to ascertain the contribution of PAHs to the SML via atmospheric wet deposition. Samples were analyzed for a suite of 16 PAH compounds and enrichment factors in the SML, rainfall loading and water-particle partitioning between the particulate and dissolved phases have been determined.

2. Material and methods

2.1. Sample collection

Sampling was conducted on the 19th October (S1), 20th October (S2) and 19th December (S3) 2005 prior to and after a significant rainfall events of more than 2 mm precipitation. Sampling was conducted at a distant of 0.5 km from the coastline in conditions of low maritime traffic and calm sea-surface conditions, at a wind speed of less than 4 m s⁻¹. It has been reported that at wind speeds greater than 4 m s⁻¹ the SML can be disturbed by wave motion (Romano and Garabetian, 1996).

Approximately 1 L of SSW (depth 1 m) and SML samples were collected before rainfall and immediately after a rainfall event. The SML was collected using the glass plate technique (Harvey and Burzell, 1972) and stored in a glass container. The glass plates, Teflon wipers, stainless steel funnel and glass containers were cleaned thoroughly with acetone prior to sampling. SSW samples were collected by a Teflon pump and Teflon-lined tubings. Each SML sample took approximately 45 min to collect. Sample collection after a rainfall event was started after rainfall had completely ceased so as to prevent any disturbance of the microlayer from raindrops.

All samples were transported back to the laboratory packed in an icebox. Water samples were filtered using a 12 V DC Teflon pump, upon returning to the laboratory, with pre-cleaned Whatman GF/A filters (1.6 µm, 47 mm i.d.). The filters were wrapped in pre-cleaned aluminum foil and kept in an air and moisture tight container. The actual volume of each samples collected was measured and recorded after filtration. Meteorological data for each rainfall event was recorded including rainfall intensity (in mm h⁻¹) and amount (in mm).

2.2. Sample treatment

Solvents and sodium sulphate were of pesticide grade. Hexane, pentane, acetone, dichloromethane were purchased from Tedia (Fairfield, OH, USA). Purified water (DI water) was obtained from ELGA PureLAB UHQ

system (Veolia Water Systems, High Wycombe, UK). The PAH stock solution was purchased from AccuStandard (New Haven, CT, USA). Anhydrous sodium sulphate (Riedel-deHaën, Germany), Silica gel (Silicycle, UK), glass wool, pasteur pipettes and sample vials were cleaned at 450 °C for 10–16 h before use.

All glassware and sample containers were soaked in a laboratory detergent solution for 12 h, and then rinsed several times with hot tap water and DI water before being dried at 220 °C for 12 h. No acetone was used to rinse glassware prior to use. Whatman GF/A filters were baked for 16 h at 450 °C, wrapped in pre-cleaned aluminum foil (baked at 450 °C for 16 h) and stored in an air and moisture tight container.

All filtered water samples were extracted on the same day as collection via liquid–liquid extraction using 3 × 150 mL dichloromethane aliquots in a two liter separation funnel. The samples were shaken for 10 min and allowed to settle for a further 10 min before the water phase was transferred back to the sample container. The organic phase was collected in a 1000 mL round-bottom flask. The sample filters were extracted using the microwave-assisted extraction system (Mars X, CEM, Matthews, NC, USA) equipped with pressure and temperature sensors. The filters were unwrapped and placed into the Teflon-lined extraction vessels containing 50 mL acetone–dichloromethane (3:2, v:v). The filters were not dried prior to extraction to avoid any potential contamination. Concentrations of PAHs are given in terms of water volume, not in terms of SPM mass. The filters were extracted for 35 min at a temperature of 85 °C. All sample extracts were reduced in volume to about 2 mL using a rotary evaporator.

Clean-up columns containing 4 g of silica gel and 1 cm of anhydrous sodium sulphate were washed with 40 mL pentane. The sample extracts were then transferred on the columns and eluted with 25 mL of pentane and 25 mL of dichloromethane–pentane mixture (2:3, v:v). The final elute of 25 mL of dichloromethane–pentane mixture was collected as a single fraction in 200 mL round-bottom flasks. The cold extracts were concentrated to about 5 mL using the rotary evaporator and further concentrated to 200 µL using a gentle purified nitrogen gas stream. The extracts were then kept in sealed vials at –20 °C until ready for analysis.

2.3. Analysis

Sample analysis was conducted using a QP5050 GCMS equipped with a Shimadzu (Tokyo, Japan) AOC-20i auto sampler and a DB-5 fused silica capillary column (30 m × 0.32 mm i.d., film thickness 0.25 µm, J&W Scientific, Folsom, CA). Purified helium was used as carrier gas with a flow rate of 1.5 mL/min. Four microlitres of sample was injected into the GCMS in splitless mode with an injection time of 1 min. Injection and interface temperatures were set to 320 and 280 °C, respectively. The oven

temperature was programmed from 80 to 268 °C at the rate of 7 °C min⁻¹ and held for 1 min, 268 to 272 °C at the rate of 2 °C min⁻¹ and held for 1 min, 272 to 294 °C at the rate of 12 °C min⁻¹ and held for 1 min, 294 to 299 °C at the rate of 2 °C min⁻¹ and held for 1 min, and from 299 to 320 °C at the rate of 2 min⁻¹ and held for 5 min. The analysis was conducted in selective ion monitoring mode (SIM). The most abundant mass ions were selected for quantification, and the other two mass ions were used to confirm the identity of the following analytes: naphthalene (Naph), acenaphthylene (Aceyl), acenaphthene (Ace), fluorine (Fl), phenanthrene (Phen), anthracene (Ant), fluoranthrene (Fluo), pyrene (Pyr), benzo(a)anthracene (BaA), chrysene (Chr), benzo(b)fluoranthrene (BbF), benzo(k)fluoranthrene (BkF), benzo(a)pyrene (BaP), indeno(1,2,3,c,d)pyrene (Ind), dibenz(a,h)anthracene (DBA) and benzo(g,h,i)perylene (BP).

2.4. Quality assurance

The analytical procedure for the suspended particulate phase (SPM) was validated via the analysis of the standard reference material SRM 1941b (National Institute of Standards and Technologies) and filter paper spiked with standard solution. Recoveries range between 64% and 91% (mean 86%) for the SRM, and between 52% and 94% (mean 80%) for spiked samples. Artificial seawater was spiked with standard solution to validate the analysis of the dissolved phase (DP), and ranged between 53% and 91% (mean 74%). A lower range of recoveries was observed for naphthalene, acenaphthylene and acenaphthene. All recoveries have been validated in triplicate samples with a relative standard deviation of less than 10%. Additional SRM and spiked samples have been analyzed with the collected samples as a control for each batch of sample processed. Field and procedural blanks have been carried out through the analysis. Control standards and blanks of pure hexane were carried out for every six samples analyzed to check the performance of the analytical system during analysis.

3. Results and discussion

3.1. Levels of PAHs in the SML and SSW

Concentrations of PAHs measured prior to wet deposition are given in Table 1. The concentration of \sum_{16} PAHs in the DP for the SSW samples varied between 3.4 and 36.5 ng L⁻¹ (mean 17.5 ± 17.1 ng L⁻¹) and between 2.7 and 46.2 ng L⁻¹ (mean 18.4 ± 24.1 ng L⁻¹) for SML samples for the three sampling events. For the SPM, the concentration for the SSW samples varied between 6.7 and 30.3 ng L⁻¹ (mean 14.8 ± 13.8 ng L⁻¹), and for the SML samples, concentrations varied between 3.8 and 31.4 ng L⁻¹ (mean 15.1 ± 14.5 ng L⁻¹). The enrichment factors (EF) of individual PAH compounds in the SML relative to subsurface water for the DP and SPM were

between 0.2–7.0 (mean 1.2 ± 1.2) and 0.3–3.2 (mean 1.3 ± 0.7), respectively. The mean EF values from this study were low compared to other studies conducted in the Chesapeake Estuary (USA), Leghorn (Tyrrhenian Sea, Italy), Baltic Sea and Alexandria (Mediterranean Sea, Egypt), but more comparable to the coastal waters offshore Spain and the Venice Lagoon (Italy) (Table 2).

A high level of variability in the concentration and EF values of PAHs in the SML has been previously observed by Liu and Dickhut (1997). In particular, for coastal waters this variability may be a result of small-scale coastal processes, such as wave motions, currents, tidal cycle, water column stratification and Langmuir circulation. Such processes are known to play an important role in the formation of the SML (Hardy, 1982) and therefore in the enrichment of organic contaminants. Meteorological conditions, such as sun irradiation and precipitation (as discussed in Section 3.2), play an important role in the variability of the enrichment of organic contaminants in the SML. Manodori et al. (2005) reported that the highest EF values for PAHs were observed when sun irradiation was lowest and was linked to reduced photo-degradation that may occur with an enhanced rate in the SML during strong sun irradiation (Blough, 1997; Ehrhardt, 1997). Photo-degradation of PAHs has been studied by Shemer and Linden (2007) and was enhanced in natural waters compared to artificial solutions. The low EF values from this study conducted in a tropical region may be derived from elevated photo-degradation rates in the SML, and also enhanced evaporation rates of volatile PAH compounds from the SML.

3.2. Effect of wet deposition on the levels of PAHs in SML and SSW

Preliminary evidence that wet deposition affects the concentration of organic contaminants in the SML, was reported previously by Wurl and Obbard (2005). In the previous study, samples from the SSW and SML were collected before and after heavy rainfall events in Singapore. The concentrations of organochlorine compounds increased up by a factor of 6 (mean 4.0 ± 1.7 , $n = 6$) in the SML, but no change was evident in the SSW (mean 0.90 ± 0.4 , $n = 6$) after the rainfall event. The unfiltered SML samples collected after rainfall events appeared blackish in color, which may have originated from soot particles. In the current study, samples were filtered to determine the distribution and fate of PAHs in the SML and SSW during rainfall events (wet deposition). Concentrations of PAHs after wet deposition are shown in Table 3. The load factors (LF), or the enrichment of contaminants before and after wet deposition, are given in Table 4.

There is a lack of direct measurement of the effect of rain to the SML, but it was reported that typical rain penetrates the microlayer (GESAMP, 1995). The impact of rain drops may cause partial mixing with SSW, but produced micro-bubbles through this impact can act as transport vector

Table 1

Mean concentrations in ng L⁻¹ of PAHs in the SML and SSW in the dissolved phase (DP) and suspended particulate matter (SPM) before wet deposition

	S1 (19th October 2005)		S2 (20th October 2005)		S3 (19th December 2005)	
	c _{DP}	c _{SPM}	c _{DP}	c _{SPM}	c _{DP}	c _{SPM}
<i>SML</i>						
Naph	1.3	0.50	1.0	1.7	32.0	21.0
Aceyl	0.93	0.05	0.15	0.20	4.8	1.0
Ace	0.79	0.17	0.11	0.44	1.2	2.0
Fl	0.53	0.48	0.36	0.82	0.29	0.14
Phen	0.60	1.1	0.19	0.97	0.79	2.4
Ant	0.06	0.16	0.01	0.07	0.04	0.33
Fluo	0.27	0.17	0.06	0.85	1.8	0.89
Pyr	0.38	0.32	0.10	0.76	0.18	0.6
BaA + Chr	0.36	0.19	0.09	1.9	2.1	0.97
BbF + BkF	0.30	0.22	0.20	1.2	0.72	0.57
BaP	0.25	0.22	0.32	0.49	0.82	0.79
Ind	0.06	0.01	0.05	0.13	0.69	0.39
DBA	0.33	0.09	0.03	0.25	0.65	0.34
BP	0.33	0.08	0.01	0.47	0.07	0.01
∑PAHs	6.5	3.8	2.7	10.3	46.2	31.4
<i>SSW</i>						
Naph	2.3	1.2	0.65	0.80	22.8	22.7
Aceyl	2.0	0.09	0.20	0.10	7.1	0.67
Ace	0.90	0.12	0.11	0.27	1.3	0.91
Fl	1.2	0.56	0.32	0.60	0.36	0.09
Phen	0.87	2.7	0.99	0.54	0.69	1.5
Ant	0.09	0.51	0.06	0.07	0.20	0.18
Fluo	0.42	0.33	0.12	0.33	1.1	0.94
Pyr	0.43	0.64	0.25	0.24	0.09	0.31
BaA + Chr	0.74	0.42	0.06	0.75	0.92	1.4
BbF + BkF	0.96	0.35	0.18	0.87	0.36	0.44
BaP	0.80	0.26	0.35	0.96	0.58	0.49
Ind	0.27	0.01	0.01	0.22	0.25	0.57
DBA	0.71	0.04	0.03	0.33	0.76	0.12
BP	0.96	0.08	0.05	0.57	0.01	0
∑PAHs	12.7	7.3	3.4	6.7	36.5	30.3

Table 2

Concentration and enrichment factors (EF) of PAHs in the sea-surface microlayer for different regions of the world

Area	Year	Concentration (μg L ⁻¹)		EF	Reference
Chesapeake Estuary	1994–1995	∑PAHs, part	0.045–8.5	5–4000	Liu and Dickhut (1997)
		∑PAHs, diss	0.055–1	1–20	
Baltic Sea	1992–1998	∑PAHs, part + diss	0.0045–0.053	1.6–12	Witt (2002)
Leghorn – Tyrrhenian Sea, Italy	1999	∑PAHs, part	0.8–154	1.5–113	Cincinelli et al. (2001)
		∑PAHs, diss	0.2–15.2	1.4–40	
Barcelona, Spain	2001–2002	∑PAHs, part	0.003–0.031	0.2–18.4	Guitart et al. (2007)
		∑PAHs, diss	0.005–0.042	0.7–5.1	
Banyuls-sur-Mer, Spain	2001–2002	∑PAHs, part	0.002–0.063	0.4–7.7	Guitart et al. (2007)
		∑PAHs, diss	0.003–0.026	0.5–3.2	
Venice Lagoon, Italy	2001–2003	∑PAHs, part	0.03–0.16	3.6–17.1	Manodori et al. (2005)
		∑PAHs, diss	0.0083–0.14	0.5–1.8	
Alexandria, Egypt	2002	∑PAHs, part + diss	0.1–0.52	3–19	El Nemr and Abd Allah (2003)
Singapore	2005	∑PAHs, part	0.004–0.031	0.3–3.2	Current study
		∑PAHs, diss	0.003–0.046	0.2–7	

for surface-active material back to the surface to re-form the SML rapidly. Smaller rain drops (<1 mm) can form a

thin layer of lower density on top of the microlayer and stabilize the SML (GESAMP, 1995).

Table 3

Mean concentrations in ng L⁻¹ of PAHs in the SML and SSW in the dissolved phase (DP) and suspended particulate matter (SPM) after wet deposition

	S1 (19th October 2005)		S2 (20th October 2005)		S3 (19th December 2005)	
	C _{DP}	C _{SPM}	C _{DP}	C _{SPM}	C _{DP}	C _{SPM}
<i>SML</i>						
Naph	1.6	1.1	1.7	0.75	41.5	35.2
Aceyl	1.2	3.1	0.27	0.14	9.3	11.8
Ace	2.3	3.2	0.15	0.26	7.3	0.8
Fl	5.4	6.5	0.52	0.71	0.43	0.1
Phen	33.8	66.5	0.59	0.85	0.49	4.9
Ant	2.6	6.7	0.04	0.03	0.13	0.69
Fluo	35.8	118.8	0.12	1.1	0.91	1.8
Pyr	19.9	48.9	0.21	0.72	0.21	1.2
BaA + Chr	60.4	266.8	0.12	3.2	2	2.4
BbF + BkF	47.9	275.1	0.21	2.1	0.81	0.92
BaP	18.4	127.2	0.38	0.32	1.1	1.3
Ind	15.4	94.4	0.01	0.35	1.2	0.74
DBA	4.9	70.9	0.03	1.1	1.4	0.32
BP	28.4	188.1	0.03	1.2	0.32	0.02
ΣPAHs	278.0	1277.3	4.4	12.8	67.1	62.2
<i>SSW</i>						
Naph	2.4	0.68	0.65	2.0	35.2	14.0
Aceyl	0.84	0.51	0.81	0.15	4.2	0.36
Ace	0.45	0.56	0.17	0.44	2.7	0.98
Fl	1.1	2.4	0.38	0.57	0.85	0.1
Phen	4.2	22.2	0.12	3.2	1.2	1.9
Ant	0.39	2.3	0.04	0.3	0.22	0.42
Fluo	1.7	46.1	0.06	1.4	4.5	0.85
Pyr	2.3	16.9	0.11	1.4	0.71	0.63
BaA + Chr	1.0	70.4	0.03	1.0	3.9	1.0
BbF + BkF	0.56	52.3	0.11	0.74	0.43	0.37
BaP	0.22	20.8	0.15	0.31	0.28	0.57
Ind	0.04	13.7	0.01	0.08	2.1	0.25
DBA	0.28	3.2	0.04	0.2	5.3	0.08
BP	0.17	29.2	0.03	0.29	0.06	0.01
ΣPAHs	15.7	281.3	2.7	12.1	61.7	21.5

Table 4

Load factors of PAHs in the SML and SSW after precipitation

	S1 (19th October 2005)				S2 (20th October 2005)				S3 (19th December 2005)			
	SML		SSW		SML		SSW		SML		SSW	
	Diss	Part	Diss	Part	Diss	Part	Diss	Part	Diss	Part	Diss	Part
Naph	1.2	2.2	1.0	0.6	1.7	0.4	1.0	2.5	1.3	1.7	1.5	0.6
Aceyl	1.3	62.0	0.4	5.7	1.8	0.7	4.1	1.5	1.9	11.8	0.6	0.5
Ace	2.9	18.8	0.5	4.7	1.4	0.6	1.5	1.6	6.1	0.4	2.1	1.1
Fl	10.2	13.5	0.9	4.3	1.4	0.9	1.2	1.0	1.5	0.7	2.4	1.1
Phen	56.3	60.5	4.8	8.2	3.1	0.9	0.1	5.9	0.6	2.0	1.7	1.3
Ant	43.3	41.9	4.3	4.5	4.0	0.4	0.7	4.3	3.3	2.1	1.1	2.3
Fluo	132.6	698.8	4.0	139.7	2.0	1.3	0.5	4.2	0.5	2.0	4.1	0.9
Pyr	52.4	152.8	5.3	26.4	2.1	0.9	0.4	5.8	1.2	2.0	7.9	2.0
BaA + Chr	167.8	1404.2	1.4	167.6	1.3	1.7	0.5	1.4	1.0	2.5	4.2	0.7
BbF + BkF	159.7	1250.5	0.6	149.4	1.1	1.8	0.6	0.9	1.1	1.6	1.2	0.8
BaP	73.6	578.2	0.3	80.0	1.2	0.7	0.4	0.3	1.3	1.6	0.5	1.2
Ind	256.7	9440.0	0.1	1370.0	0.2	2.7	1.0	0.4	1.7	1.9	8.4	0.4
DBA	14.8	787.8	0.4	80.0	1.0	4.4	1.3	0.6	2.2	0.9	7.0	0.7
BP	86.1	2351.3	0.2	365.0	3.0	2.6	0.6	0.5	4.6	2.0	6.0	0.0
ΣPAHs	42.8	336.1	1.2	38.5	1.6	1.2	0.8	1.8	1.5	2.0	1.7	0.7

The enrichments of ΣPAHs in the SML of the dissolved and particulate phase increased after the rainfall events to a

range of 1.1–18.5 (mean 7.1) and 1.1–4.5 (mean 2.83), respectively. This indicates that the SML is rapidly

re-formed after the rainfall events. Indeed, Dragevic and Pravdic (1981) reported a rapid formation of organic surface films within <1 s and suggested continuous renewal of surface films on the ocean, at least under moderate wind conditions below 4 m s^{-1} (Romano and Garabetian, 1996).

LF values for dissolved PAHs were significantly higher for sampling events S1 (paired t -test; $p = 0.0017$) and S2 ($p = 0.033$) for the SML compared to SSW, but less significant for S3 ($p = 0.056$). For the particulate phase, LF values were higher for sampling events S1 ($p = 0.045$) and S3 ($p = 0.049$) for the SML compared to SSW, but not for S2 ($p = 0.147$). The LF values for the particulate phase of PAHs were significantly higher ($p < 0.05$) than for the dissolved phase, except for the SML during sampling events S2 ($p = 0.212$) and S3 ($p = 0.344$).

LF values were higher by a magnitude of three during the sampling event S1 compared to sampling events S2 and S3. In particular the compounds Fluo, Pyr, BaA + Chr, BbF + BkF, BaP, Ind, DBA and BP were enriched during wet deposition for the sampling event S1 with LF values higher than 150. To explain the high variability in the LF values, or the effect of wet deposition of organic contaminants on the SML and SSW, rainfall data for the sampling events has been obtained from a 4 km northeastern located weather station at the National University of Singapore. The rainfall event on the 19th October 2005 was heaviest with a rain rate of 56.4 mm h^{-1} (total rainfall 8.4 mm). The rainfall events on 20th October and

19th December 2005 were much lighter with rainfall rates of 7.6 and 2.9 mm h^{-1} , respectively (total rainfall 2.8 and 2.2 mm, respectively). It is apparent that the LF value is dependent on rainfall intensity and a higher wash-out of atmospheric particulate results in the higher enrichment of particulate-associated PAH contamination in the SML and SSW. The SML is strongly affected by floating particulates deposited during a rainfall event (Fig. 1), but particulates may aggregate to sink deeper or mix with deeper waters via turbulence at the water surface.

The origin of air masses is likely to be another factor affecting the variability of LF values. Air mass back trajectory analysis has been performed using the HYSPLIT transport and dispersion model from the NOAA Air Resources Laboratory (Draxler and Rolph, 2003). The back trajectories (BTs) were traced for 5 days at an altitude of 500 m above sea level and are represented in Fig. 2.

The air mass from the 19th October 2005 (S1) clearly traveled over Malaysian Peninsula and Singapore for 5 days before reaching the sampling site. The air masses from the 20th October (S2) were mainly of oceanic character with terrestrial influence from Thailand and coastal areas of Sumatra. Both air masses from October 2005 originated from a low altitude and rose to 500 m within 5 days. The air mass from 19th December 2005 traveled a much further distance and originated over China at an altitude of 3500 m above sea level. Generally, the air mass was of oceanic character traveling over the South China Sea and partly over Vietnam before reaching Singapore within 5 days. Beside the high rainfall intensity, the high particulate loading to the SML during the rainfall event on 19th October 2005 may have been affected by the terrestrially sourced air mass.

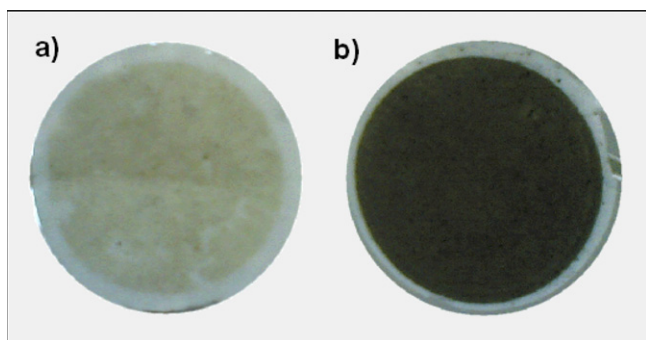


Fig. 1. Filtered SML samples collected before (a) and after (b) heavy rainfall event on 19th October 2005.

3.3. Changes of the distribution of PAHs between DP and SPM during wet deposition

The distribution pattern of PAHs between the DP and SPM phases (Fig. 3) is similar in both the SML and SSW ($p > 0.05$), except for the SML and SSW samples collected on 19 December 2005 (S3) after wet deposition ($p < 0.003$). Differences in the PAH distribution pattern before and after wet deposition in the SSW were significant for all three sampling events ($p < 0.02$). For the SML, the change

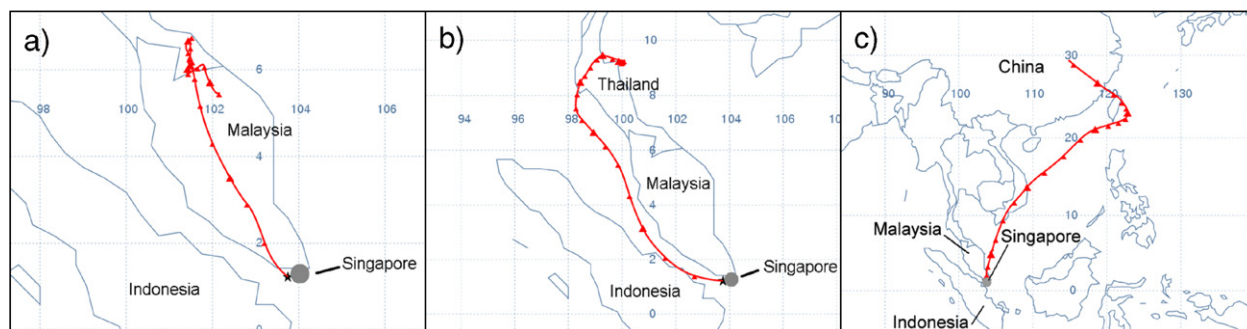


Fig. 2. Air mass back trajectories for 5 days on the 19th October (a), 20th October (b) and 19th December 2005 (c).

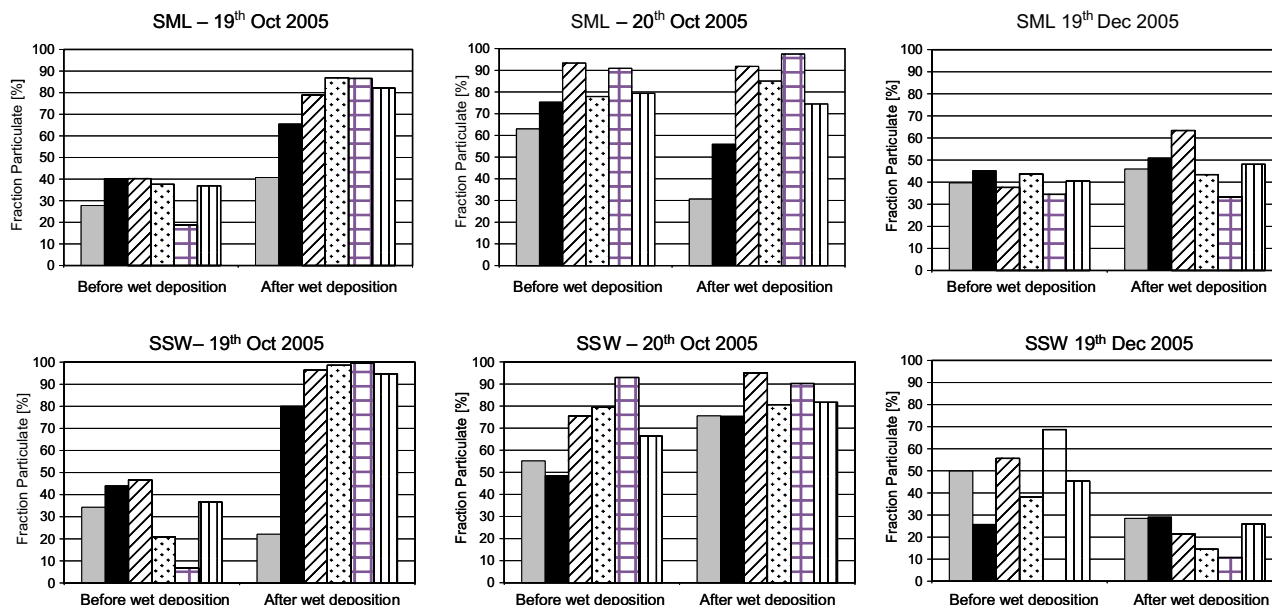


Fig. 3. Mass fraction associated to particulates of 2-ring (■), 3-ring (■), 4-ring (▨), 5-ring (▩), 6-ring (▤) and total PAH compounds (▧) in the SML and SSW on 19th October 2005.

in the distribution pattern during wet deposition was less significant on the 20th October and 19th December 2005 ($p > 0.06$), but significant during the heavy rainfall event from the 19th October 2005 ($p < 0.002$). Mass fractions in the SML after wet deposition from 19th October increased with the ring-number of individual PAH compounds (Fig. 3). PAHs associated to the SPM were dominant on 19th October (after wet deposition) and on the 20th October 2005 (before and after wet deposition) with a fraction $> 50\%$, and as high as 98% for individual PAH compounds. Prior to wet deposition, 50% of the PAHs were associated to particulates, except for the 20th October 2005 with a fraction of up to 80%.

The relatively high-fraction of SPM-associated PAHs from the 20th October 2005 prior to wet deposition may be linked to the heavy rainfall event the previous day, on which a similar, high-fraction of PAHs associated to SPM was detected after wet deposition. No rain fell during the night of 19th October 2005, and it is suggested that heavy rainfall events affect the distribution of PAHs via an increased mass fraction of PAHs in the SPM.

3.4. PAH contamination sources

The SML is a dynamic compartment in the ocean surface, where the presence of contaminants is dependent on several inputs (atmospheric dry and wet deposition, sediment resuspension, riverine discharge) and outputs (evaporation, bubble bursting, photo-degradation, sinking particulates and turbulent mixing). Evidence that wet deposition is a major pathway for the transfer of PAHs from the atmosphere to the SML is confirmed by this study. Cross-plots of the ratios of Phe/Ant versus Flu/Pyr can be used to evaluate the sources of PAH con-

tamination before and after wet deposition (Manodori et al., 2005; El Nemr and Abd Allah, 2003; Budzinski et al., 1997), and are presented in Fig. 4. It is observed that particulate samples in both the SML and SSW likely

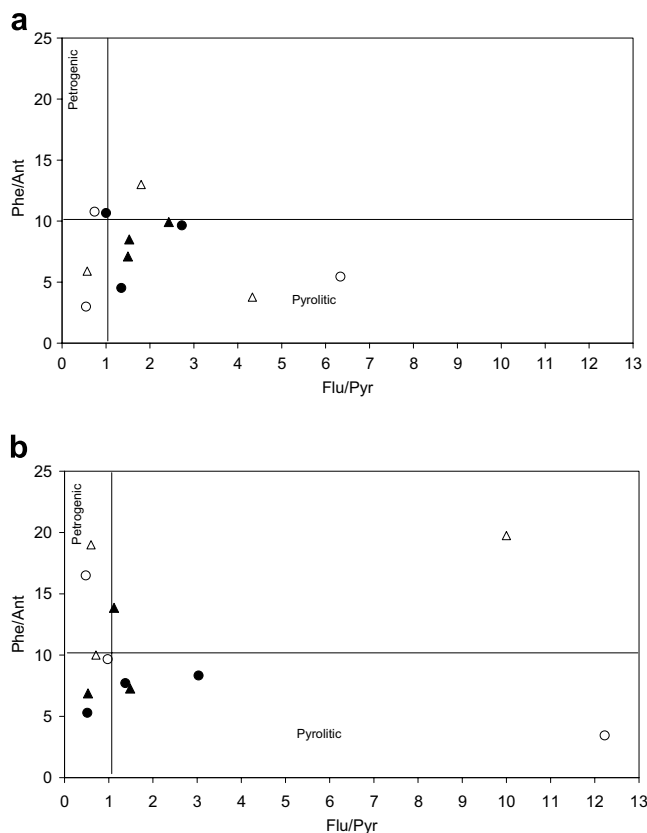


Fig. 4. Cross-plots of the Phe/Ant versus Flu/Pyr values for DP in SML (Δ) and SSW (○), and for SPM in SML (▲) and SSW (●) before (a) and after wet deposition (b).

originate from pyrolytic sources, whilst composition of PAHs in the DP are more diffuse and therefore a source cannot be readily identified. However, three samples collected before wet deposition from the DP indicate a petrogenic origin (Fig. 4a), and boating activities adjacent to the sample site are a likely source of petrogenic PAHs. Samples collected after wet deposition suggests a pyrolytic origin, despite the proximity of a large petrol refinery within 3 km of the sample site. BP and BaP has been associated with terrestrial inputs from rivers and estuaries (Budzinski et al., 1997). High concentrations of BP were found in the samples collected after the rainfall event on 19th October 2005, and may originate from a higher discharge of urban-runoff caused by the heavy rainfall event, but relatively high concentrations of these compounds have been also detected in rainwater samples over Singapore (Basheer et al., 2001) contributing to the increasing concentrations during rainfall events.

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